A Mass Spectrometric Study of the Carbon-Carbon Dioxide Reaction

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INTRODUCTION

Carbon dioxide can react with carbon to form carbon monoxide. This is a reversible reaction which can be represented by the equation

$$C + CO_2 \rightleftarrows 2\ CO \quad .$$
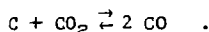
Factors such as the type of carbon used and the impurities present in the carbon can drastically affect the rate of the reaction.

There have been a number of mechanisms proposed for this reaction (1-10). Most of these mechanisms postulate the formation of a surface oxide or complex as an intermediate step in the reaction. There is some agreement that the surface complex does not exist at temperatures above 800°C. and, hence, does not play an important role in the reaction carried out at higher temperatures.

In order to investigate the carbon-carbon dioxide reaction with particular emphasis on the role of any surface oxide intermediate, certain factors must be considered. Since the surface oxide is believed to be unstable at temperatures greater than 800°C., the reaction should be carried out at temperatures as much below this point as possible in order to maximize the probability of surface oxide formation. The amount of gas necessary to completely cover a carbon surface is relatively small (approximately 10 micromoles per square meter for carbon monoxide as the adsorbate (11)). Therefore, the relative change in pressure resulting from the formation of a given amount of surface complex can be maximized by operating at low pressures. A sufficient number of the reaction variables have to be measured to be able to compute a complete material balance throughout the progress of the reaction. Furthermore, the measuring system has to be sensitive enough to detect small amounts of reaction in order to minimize the effect of changing surface area during the course of the reaction.

For this investigation, carbon was reacted with carbon dioxide at temperatures from 400°C. to 700°C. and at starting pressures from 2.7 to 16 microns of mercury. The reaction was followed by monitoring the partial pressures of carbon dioxide and carbon monoxide using a mass spectrometer. The sensitivity of the mass spectrometer was sufficiently great to detect surface coverages of 0.01 per cent and reaction of 0.001 per cent of the carbon in the system.

APPARATUS AND EXPERIMENTAL PROCEDURE

Figure 1 shows a schematic picture of the low pressure reactor. The tubing in the system is $1\frac{1}{4}$ inches in diameter; the volume of the system is 16.6

liters. The fused silica reactor tube is set at an angle of 45° so that thermal convection will aid in the mixing of the reacting gases. The system can be evacuated to pressures of 10^{-5} mm. Hg using an oil diffusion pump which is connected to the reactor by stopcock S_1.

There are three pressure measuring devices - an ionization gauge, a thermocouple gauge and a McLeod gauge. Since the mass spectrometer measures partial pressure of all gases present, it also can be used as a pressure measuring device.

The reaction system can be isolated from the mass spectrometer by stopcock S_4. The reaction gases are admitted to the reaction system through stopcocks S_2 and S_3.

The carbon sample is placed in a 1 x 5 cm. fused silica tube sealed at one end. The sample container can be lowered into the reaction tube through a sample port in the upper part of the apparatus. The sample container rests on a fused silica tube, which extends upwards from the bottom of the reaction tube. This support tube also contains a chromel-alumel thermocouple. The cap for the upper port in the reactor contains a Pyrex optical-flat window through which the sample can be observed.

The sample is heated by a 1 KW tube furnace which surrounds the reaction tube. The furnace is $8\frac{3}{4}$ inches long. The temperature of the furnace, as indicated by the thermocouple in the sample support tube, is regulated by an automatic controller-recorder.

The mass spectrometer has been modified so that the reactor can be directly connected to the inlet leak of the spectrometer analyzing tube. Under the conditions used in this investigation, the spectrometer bled off less than two per cent of the total gas present during the course of a run.

A programmed magnetic field controller was constructed to enable the mass spectrometer to sequentially monitor the mass 44 (CO_2^+) ion beam and the mass 28 (CO^+) ion beam every 15 seconds.

In order to determine the time constant of the analyzing system, the reactor was filled with carbon monoxide to a pressure of 8 microns of mercury; and a 5 per cent increment of carbon dioxide was admitted into the reactor. By adjusting the mass spectrometer to monitor mass 44 (CO_2^+), the time taken for the 44 peak to reach a steady state gives an idea of the rate of diffusion and mixing of the gases in the reactor. It was found that the response of the spectrometer was practically instantaneous, with a steady state value obtained within 5 seconds.

The carbon used for this investigation was a highly ground sample of SP-1 spectrographic graphite*. The spectrographic graphite was ground** for 16 hours

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* The unground SP-1 sample was supplied by the National Carbon Company.

** The SP-1 sample was ground through the courtesy of Mr. S.B. Seeley of the Joseph Dixon Crucible Company.

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in a vacuum ball mill in order to increase its surface area, as described recently
by Walker and Seeley (12). After grinding, the area of the graphite wear dust was
560 m.^{2}/g. The grinding process introduced ca. 5 per cent iron into the sample.

The carbon sample was heated to a temperature of 850°C. in vacuum for
3 hours prior to each run. This pretreatment insured that the gases evolved upon
the heating of the sample at the end of each run were a result of the reaction and
not the past history of the carbon.

RESULTS AND DISCUSSION

Figure 2 shows typical data obtained from the mass spectrometer during
a run. This figure illustrates how the spectrometer is calibrated for carbon
monoxide,and carbon dioxide just prior to and immediately after the reaction
period. Also it shows removal of the surface complex as carbon monoxide upon
outgassing the sample following the reaction.

Figure 3 presents the results of this run after data reduction. The
reaction rates could be duplicated to within 5 per cent in runs at the same temper-
ature. It was found that the rate of carbon monoxide formation was slightly less
than twice the rate of carbon dioxide consumption. This departure from a two to
one ratio involves a small amount of carbon monoxide "tied" to the surface of
the carbon sample. This complexed carbon monoxide could be recovered by heating
the carbon in a vacuum at higher temperatures after the run.

Figure 4 shows the plots of log carbon dioxide concentration versus time
for the reaction over the temperature range 400° to 700°C. The experimental data
very closely follow a log function throughout the course of the reaction at all
temperatures. This indicates that the rate of reaction of carbon dioxide is first
order with respect to the carbon dioxide pressure throughout the entire reaction
at all temperatures investigated.

With the experimental conditions used in this investigation, two factors
can affect the reaction rate, chemical reactivity and the rate of diffusion of the
reacting gas through the unconsolidated carbon sample. When the rate of diffusion
is large compared to the rate of chemical reaction, the latter will completely
control the over-all rate of reaction. Under these conditions the rate of
reaction per unit surface area will not be affected by variation in sample size.
However, if the rate of chemical reaction is greater than the rate of internal
diffusion, an increase in weight of sample reacted will not have a proportional
effect on the over-all rate of reaction. Therefore, the rate of reaction per
unit surface area will decrease. It was found that the rate of reaction per unit
surface area varied with weight of sample reacted.

Table 1 gives the rate constants* for the decrease in carbon dioxide
pressure with time per unit surface area versus the sample size.

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* In a constant pressure reaction system or a constant volume reaction system
where only a small amount of the total gas is heated, the rate data obtained should
be normalized to a constant concentration basis. For this investigation, 27°C.
was taken as the standard temperature. Therefore, the experimental rate constants
were multiplied by the ratio of the temperature of the reaction to the standard
temperature in degrees absolute.

TABLE 1

EFFECT OF TOTAL SURFACE AREA OF GRAPHITE WEAR DUST ON THE
RATE CONSTANT FOR THE DECREASE IN CARBON DIOXIDE PRESSURE IN
THE REACTION $C + CO_2 \rightarrow 2\ CO$

Temperature °C.	Rate Constant k, sec.$^{-1}$ m.$^{-2}$ x 10^6	
	53 m.^{2} Surface Area	133 m.^{2} Surface Area
400	1.21	1.12
500	28.7	23.6
650	116.7	89.0

From Table 1 it can be seen that as the reaction temperature decreases the rate constant becomes less dependent on the sample size. This indicates that there was some diffusion control throughout most of the temperature range investigated, with chemical control being almost complete below ca. 450°C. At the lower temperatures, the activation energy approaches a value of 38 kcal./mole.

Figure 5 shows the per cent of the carbon surface that was covered by complex at the end of a reaction versus reaction temperature. It can be seen that the amount of complex formed increases to a maximum in the 600°C. region and then rapidly decreases. The reason for this trend is apparent when one refers to Figure 2. It is noted that in the outgassing of the sample following a run, the complex which has been formed is quite stable until the carbon is heated to temperatures greater than 600°C. The temperature at which the complex was formed was found to have little effect upon its stability.

The carbon monoxide surface complex could be formed as a product of the carbon dioxide reaction,

$$C + CO_2 \rightarrow CO + C(O)$$
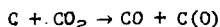
or it could be due to the chemisorption of carbon monoxide on the surface of the sample,

$$CO \rightarrow (CO)$$
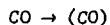
Here $C(O)$ represents a complex formed upon reaction of CO_2, while (CO) represents chemisorbed carbon monoxide. By exposing the carbon surface to carbon monoxide, the rate of chemisorption can be studied. It was found that the rate of chemisorption increased to a maximum around 600°C. Table 2 shows the amount of carbon monoxide chemisorbed at 600°C. for various pressures and lengths of time. The coverage of 0.125 per cent of the surface in three days indicates that only a small fraction of the total surface will chemisorb carbon monoxide. The relatively small difference between the amount of surface coverage at a pressure of 2.7 microns of carbon monoxide for 30 minutes and a 24 micron pressure of carbon monoxide for 3 days indicates that the majority of this small area is rapidly saturated with chemisorbed carbon monoxide. The chemisorbed carbon monoxide could be recovered by heating the carbon to temperatures greater than 600°C.

TABLE 2

PER CENT OF WEAR DUST SURFACE COVERED WITH CHEMISORBED CARBON MONOXIDE AT 600°C.

	Pressure, (microns of CO)		
Time	2.7	8	24
30 min.	0.054	0.065	0.074
3 days	-	-	0.125

Since the chemisorbed carbon monoxide exhibits the same characteristics as the complex formed during the carbon dioxide reaction, it appears that the complex is chemisorbed carbon monoxide. This chemisorption is a side reaction and does not play a role in the mechanism of the conversion of carbon dioxide to carbon monoxide.

It is recalled that, as a result of the grinding process, the carbon sample used in this investigation contained ca. 5 per cent iron. A ground sample from which the iron was removed did not chemisorb any measurable amount of carbon monoxide. The iron had a very strong catalytic effect on the reactivity of the carbon. The "iron-free" sample had to be heated ca. 300°C. higher than the "iron-containing" sample in order to obtain a comparable reactivity. Although the experimental data indicate that the carbon dioxide is converted to carbon monoxide with no measurable build-up of any intermediate products, the great difference in reactivity between the original "iron-containing" sample and the "iron-free" sample indicates that the iron must play an important role in the reaction mechanism.

A possible mechanism by which the iron could catalyze the reaction would be,

$$y \ CO_2 + x \ Fe \rightleftarrows Fe_xO_y + y \ CO \qquad (1)$$

$$Fe_xO_y + y \ C \rightleftarrows x \ Fe + y \ CO \ . \qquad (2)$$
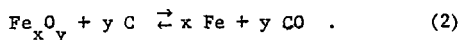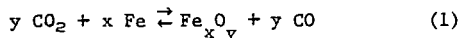
Both steps one and two in this mechanism are reversible reactions. The equilibrium constant of step one is pressure independent and is approximately one for the range of temperatures used in this investigation. Step two is a pressure dependent reaction; operation at low pressures of carbon monoxide favors the reduction of the iron. If the rate of the forward reaction in step two is sufficiently fast to prevent a significant build-up of iron oxide, the rate of the back reaction in step one would be small. Under these conditions, only the forward reactions of step one and two would play an important role in the over-all reaction schema.

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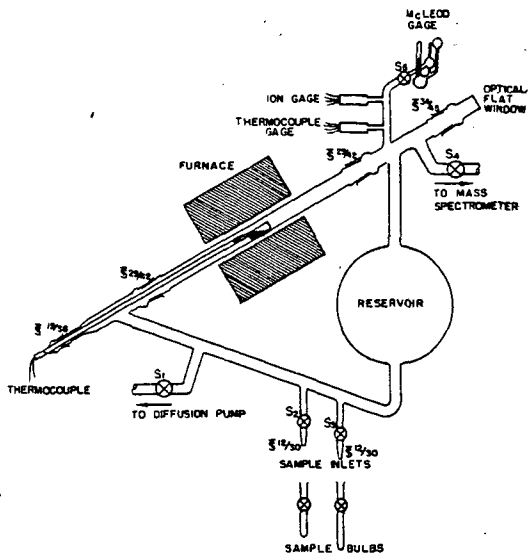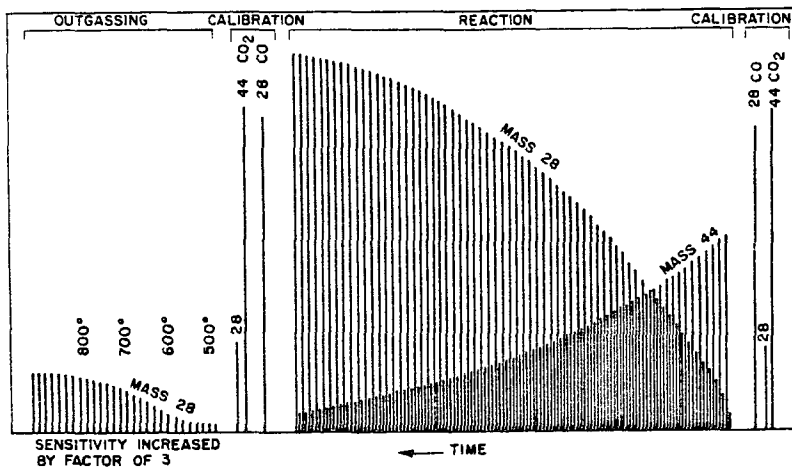
FIGURE 1 - LOW PRESSURE REACTOR
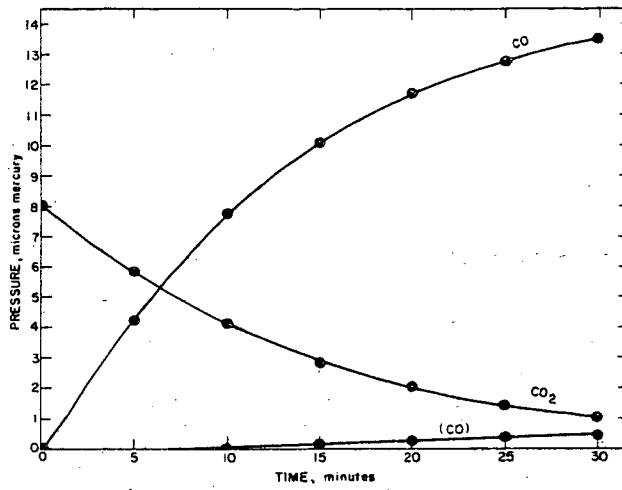

FIGURE 2 -TYPICAL MASS SPECTROMETER RECORD
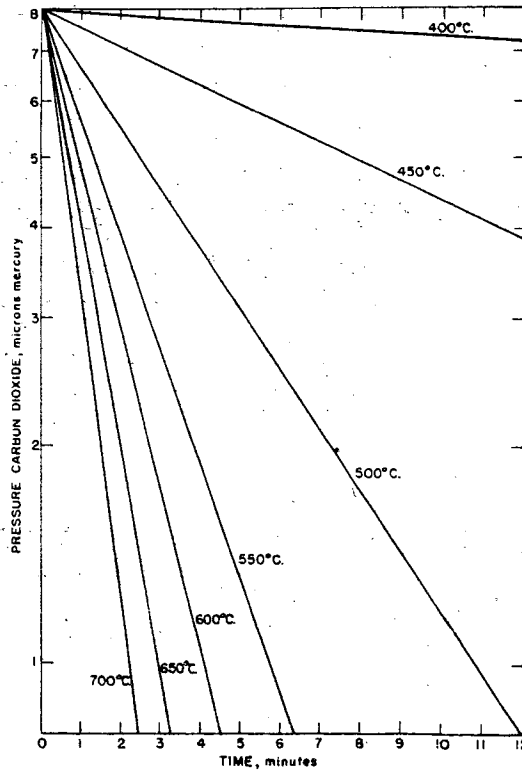
FIGURE 3 – TYPICAL REACTION CURVES
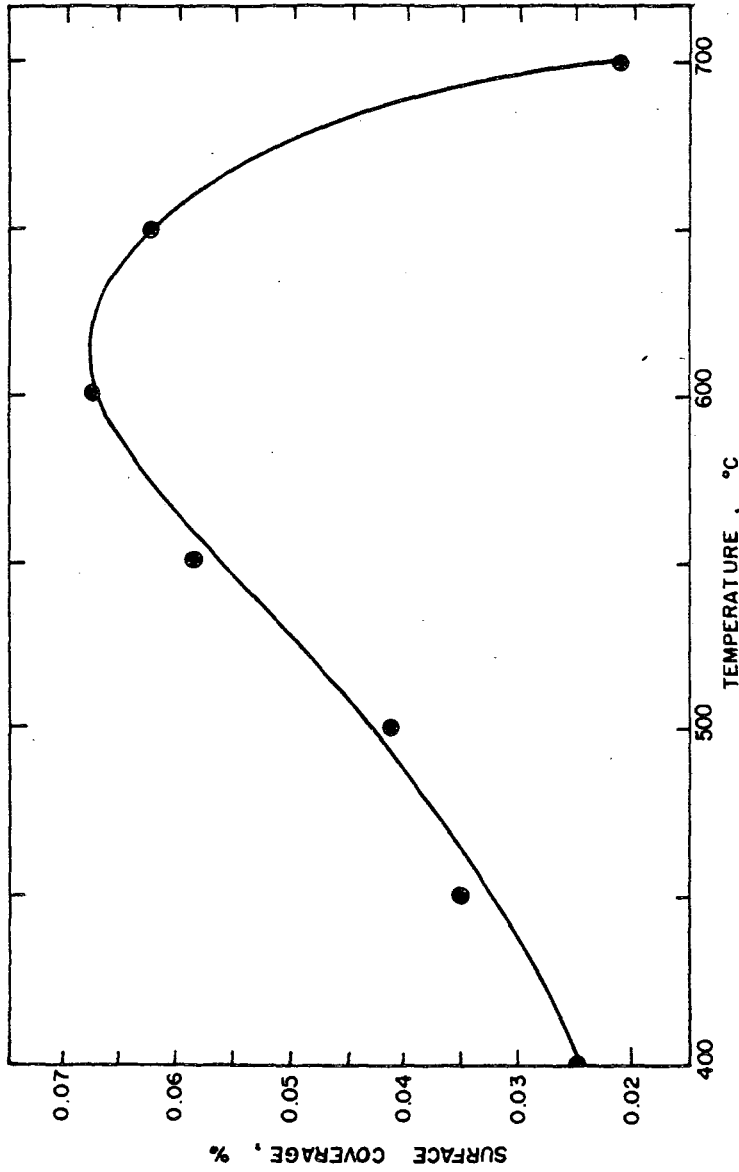

FIGURE 4 – REACTION CURVES FOR GROUND SP-1 GRAPHITE

FIGURE 5 — SURFACE COVERAGE OF OXIDE COMPLEX AT END OF REACTION VERSUS REACTION TEMPERATURE